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COMPONENT FOR PRODUCING POLYMER MIXTURES BASED ON  
STARCH, AND PROCESS FOR PRODUCING THE COMPONENT

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The invention relates to a component consisting of polyvinyl acetate and alkali water glass for producing thermoplastically deformable, biodegradable and bright polymer mixtures based on starch, with good dimensional stability in water, which can be applied for the manufacture of sheet material, semi-finished and finished products, for example for packagings, containers and articles required in horticultural nurseries, in particular growing or cultivation aids, as well as in other fields of application. The invention, furthermore, relates to a process for producing said component.

Numerous methods have become known in the last few years for producing and shaping thermoplastic starch (TPS) either alone or in the form of a polymer mixture or polymer melt or polymer blend (in the following referred to as a polymer mixture). Said methods were developed with the goal to open up new or expanded fields of application for regrowing raw materials. The basis of all inventions that have become

known heretofore is the finding that the grainy structure of native starch can be changed into thermoplastic material first with defined proportions of water and/or lower polyfunctional alcohols such as ethylene glycol, propylene glycol, glycerol, 1,3-butane-diol, diglyceride, and the respective ethers, but also with compounds such as dimethyl sulfoxide, dimethyl formamide, dimethyl urea, dimethyl acetamide, and/or other additives, through thermomechanical breakdown with the help of conventional extruders; and that such materials then can be molded.

The useful value of the extrudate and of the products produced from the latter is low. In particular, the material is highly hydrophilic.

More recent proposals are dealing with the admixture of synthetically obtained waterproof polymers such as, for example polyethylene, polypropylene, polycaprolactone, as mixing components for starch. In this connection, however, the problem arises that the compatibility between the polymer components is inadequate, and that the biodegradability and also the cost structure become unfavorable.

The prior art is extensively documented in the relevant literature. Reference is made in this connection, for example to the publication by R.F.T. Stepto et al "Injection Molding of Natural Hydrophilic Polymers in the Presence of Water", Chimia 41 (1987), No. 3, pp. 76-81, and the literature cited there, as well as, for example to patents DE 4116404; EP 0327505; DE 4038732; US 5,106,890; DE 4117628; WO 94/04600; DE 4209095; DE 4122212, EP 0404723; and EP 407350.

In DE 40 38 732, the starch plasticized with water and glycerol is processed in the extruder to a polymer mixture predominantly with polyvinyl acetate. The extrudate exhibits superior resistance to water as compared to TPS. With higher amounts of starch components, the extrudate or the bottles produced therefrom take on a yellowish to brownish color. This limits the starch component to below 50%.

A slightly acid to neutral component consisting of polyvinyl acetate and water glass has already been proposed (DE 195 33 800) in which a polymer mixture of starch and a hydrophobic polymer, e.g. polyvinyl acetate, can be

extruded. The component is produced from water glass and polyvinyl acetate as well as, if need be, further acid components for adjusting the pH, by the extrusion process with intensive mixing. It has been found that even only minor additions of said component lead to a significant qualitative improvement of the extrudate and of the products manufactured from the latter. As compared to the prior art, native starch can be used in considerably greater amounts without or with only minor discoloration and while maintaining or enhancing the dimensional stability in water. The component obviously contributes to the fact that the two phases, which are not compatible in mixture per se, render the hydrophilic thermoplastic starch and the hydrophobic polymer miscible to a certain degree.

Further tests have shown that the quality of the final products has to be improved even further with respect to dimensional stability in water and strength. In particular, it has not been possible to manufacture thin sheet materials with a thickness of below about 300  $\mu\text{m}$ .

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Starting with the goal to make even more use of regrowing raw materials for the economical manufacture of products that are compatible with the environment, the present invention developed based on the problem of proposing a component with which it is possible to extrude from thermoplastic starch and a hydrophobic polymer, for example polyvinyl acetate, qualitatively higher valued, thermoplastically moldable and biodegradable polymer mixtures, as well as on the problem of proposing a process for producing said component from polyvinyl acetate and alkali water glass.

The component is obtained according to the invention by hydrolizing and saponifying the polyvinyl acetate in the batch process in the presence of catalytic additions of low-molecular organic mono-, di- and trihydroxyl compounds (e.g. methanol, ethanol, ethylene glycol, glycerol) with a continuous addition of basically reacting compounds and the alkali silicate.

The component contains organosilicates of high homogeneity and fineness consisting of partially saponified polyvinyl acetate and alkali silicate solution, additional

reaction products produced in situ, as well as residues of the catalyst employed in the production of said component.

Characteristic of the way in which the reaction is controlled is that the polyvinyl acetate is loaded first in an about 50% suspension with the catalyst, and that the basic compounds are added under thorough mixing before the alkali silicate solution is added, or together with the latter.

It has been found that it is possible with said component to extrude polymer mixtures with high starch proportions analogous to DE 195 33 800. It is shown in the examples of execution in greater detail that the products manufactured from said polymer mixtures have a distinctly higher quality with respect to a number of parameters. In particular, it is possible already now to produce sheets with a thickness of less than 100  $\mu\text{m}$ .

Various modifications have already been found.

Especially if the polyvinyl is presaponified with calcium hydroxide, a component is formed with which

biodegradable polymer mixtures of high strength can be produced. The best values to date were obtained with calcium hydroxide and sodium disilicate (instead of water glass).

The quality of the final products is enhanced even if native starch and vinylacetate or polyfunctional silane (e.g. Dynasilane GLYMO of the Hüls Company) are added in the manufacture of the component in small amounts.

The component is solid at room temperature and a structured liquid at above 40°C. Following removal from the mixer, excess water can be removed by centrifuging. A residual moisture of 35% to 40% usually remains in the product. The catalyst employed is contained in said residual moisture about proportionally to the amounts of catalyst and liquid used.

The invention is explained in greater detail in the following with the help of a number of exemplified embodiments.

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The various components were produced in a discontinuously operating solid/liquid mixer of the firm Gebrüder Lödige Maschinenbau GmbH. The mixer is equipped with centrifuging gear controllable via the speed (about 350 rpm max.), and with a blade head operating at constant speed. The mixture was heated via the twin jacket of the mixer by means of a pressure-superposed tempering system, or with direct steam.

After the reaction temperature of 120° to 140°C was reached, reaction times of from 1 to 2 hours were required.

The following feed stock was charged: 55% polyvinyl acetate suspension; 99.5% glycerol; 40% Na water glass 37/40; as well as NaOH and/or  $\text{Ca}(\text{OH})_2$ .

For determining the quality, polymer mixtures based on polyvinyl acetate and starch each containing 10% of the respective component used were extruded analogous to DE 195 33 800, and test specimens and flat sheets were produced from said polymer mixtures. The mass ratio of starch to polyvinyl acetate amounted to 3:1 in all tests without change.

The degree of swelling (SW in %) and the solubility (SO in %) were determined on the test specimens, which were stored in water at room temperature for a period of 24 hours. In this connection, the degree of swelling corresponds with the quotient based on the mass difference of undried swollen test specimen ( $m_{sw}$ ) and the same dried test specimen prior to swelling ( $m_A$ ) relative to the starting mass of the dry test specimen prior to swelling ( $m_A$ ):

$$SW = \frac{m_{sw} - m_A}{m_A} \quad (\text{in } \%).$$

The solubility is calculated based on the mass of the dry starting specimen ( $m_A$ ), reduced by the mass of the watered dried specimen ( $m_w$ ) and related to the mass of the dried starting specimen:

$$SO = \frac{m_A - m_w}{m_A} \quad (\text{in } \%).$$

The tensile strength ( $\sigma$  in MPa), elongation ( $\epsilon$  in %) and the E-modulus (in MPa) were determined on test specimens in the form of shoulder rods ( $L = 75$  mm;  $W_{\text{shoulder}} = 13$  mm;  $W_{\text{bridge}} = 4$  mm). Said rods were punched out at 130°C

from extruded flat sheets, and stored over 24 hours at 50% relative air humidity. The test speed came to 200 mm/min; the measurements were carried out in accordance with ISO 527.

The numerical values specified in the table (see below) represent average values based on several comparable measurements.

#### Example 1

1600 g polyvinyl acetate suspension and 120 g glycerol was loaded by weight in an unheated laboratory mixer and, under stirring with the centrifuging gear (n 300-350 rpm), heated to the reaction temperature of 140°C. 900 g of the sodium water glass solution, enriched with 171 g sodium hydroxide, was continuously metered into the hot reaction medium via a micro-dosing pump against the pressure existing in the interior of the mixer, said pressure corresponding with the temperature and the water content. The dosing rate was selected in such a way that the desired reactions were substantially completed when the dosing was stopped. In the present example, the metering and reaction time

amounted to 2 hours. In addition to the centrifuging gear, the blade head was switched on throughout the entire metering time as well. Following metering of the sodium glass water solution, flushing was carried out with 0.25 N. soda lye in order to feed the rest of the water glass into the reaction mixture.

The properties of the extruded polymer mixture are specified in the following table under Example 1.

For comparison purposes, a component was prepared analogous to DE 195 33 800, but also by the batch process (thus under superior conditions). The properties of the extruded polymer mixture are contained in the following table under Example 0.

It is obvious that the values of the extruded polymer mixture prepared with the component produced according to the invention are enhanced. Most of all, however, it was possible to produce substantially thinner sheets than heretofore.

### Example 2

Same as Example 1; however, instead of the amount of sodium hydroxide added to the sodium water glass in 1, an equimolar amount of calcium hydroxide was added to the reaction batch. Following heating, the water glass was metered into the mixture with the micro-dosing pump and the reaction was completed according to the procedure described in Example 1.

### Example 3

The calcium hydroxide is added by weight to the polyvinyl acetate/glycerol mixture and intimately homogenized. The preparation is subsequently heated to the reaction temperature and maintained at said temperature for 1 hour. Metering of the sodium water glass was subsequently carried out as in Examples 1 and 2.

The degree of presaponification can be varied by varying the reaction time and reaction temperature as well as the concentration of the basic starting substances.

The resistance to water of the polymer mixture is enhanced by using calcium hydroxide and particularly by

verifying the presaponification (see table, Examples 2 and 3).

#### Example 4

5% native potato starch based on the weighed amount of polyvinyl acetate suspension was added to the reaction batch prior to saponification, and reacted as described in Example 1. A certain deterioration occurred as compared to the values obtained in Example 1 (table, Example 4).

#### Example 5

5% potato starch and 0.5% vinylacetate based on the weighed amount of the polyvinyl acetate suspension was added to the reacted reaction product obtained from polyvinyl acetate, sodium hydroxide and sodium water glass, and an ester interchange was carried out for 1 hour at 40°C. The product properties showed a substantial improvement (table; Example 5).

#### Example 6

Adding 5% of a polyfunctional silane (Dynasilane GLYMO, Hüls Company) based on the mass of silicate

introduced into the component by the sodium water glass has a positive effect on the properties of the extruded compound as well (see table; Example 6). Therefore, the weighed portion of silane was admixed to the finished component at a temperature of below 100°C. The mass was heated to 120°C and stirred for **20** minutes at said temperature.

#### Example 7

A further possibility of influencing the spectrum of the properties of extruded starch/polyvinyl acetate mixtures becomes accessible through the synthesis of a component consisting of polyvinyl acetate suspension partially saponified with calcium hydroxide, and sodium disilicate. The composition of the reaction batch is selected in this connection in such a way that it corresponds with the degree of saponification and the silicate content of the component according to Example 1. The polyvinyl acetate suspension, the calcium hydroxide and the sodium disilicate are mixed by weight, heated to the reaction temperature, and maintained at said temperature over a period of time (2 hours) conforming to the metering of the water glass (table; Example 7).

Table: Property values of the polymer mixtures extruded with the different components (Examples 1 to 7) as defined by the invention, and with the comparative component (Example 0).

Example	Components	SW (%)	SO (%)	$\sigma$ (MPa)	$\varepsilon$ (%)	E-modulus (MPa)
0	Recipe according to DE 195 33 800	142	20	8.0	80	76
1	NaOH dissolved in sodium water glass solution	113	16	10.9	74	88
2	Ca(OH) <sub>2</sub> , without pre-saponification	95	17	9.8	91	126
3	Ca(OH) <sub>2</sub> with pre-saponification	90	16	10.5	77	155
4	with potato starch	129	21	6.7	118	23
5	with potato starch and vinyl acetate	105	14	12.6	62	293
6	with dynasilane GLYMO	106	15	13.4	75	216
7	with Ca(OH) <sub>2</sub> and sodium disilicate	87	15	15.4	56	464